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## THE THERMODYNAMIC TREATMENT OF CONCENTRATED SOLUTIONS, AND APPLICATIONS TO THALLIUM AMALGAMS.

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The very complete investigation by Richards and Daniels<sup>1</sup> of the electromotive and thermal properties of thallium amalgams, and Hildebrand and Eastman's<sup>2</sup> study of the vapor pressure of mercury from such amalgams at 325°, together furnish unusually satisfactory material for illustrating the exact thermodynamic treatment of concentrated solutions.

Having made several calculations from these data, for the purpose of such illustration, it has seemed to us that their publication might be of interest. For, while the fundamental methods involved here have all been described in the literature, in the study of concrete cases numerous expedients have been devised for diminishing the labor and increasing the accuracy of those calculations and extrapolations which are necessary for the complete utilization of given data. The special methods here described will be found useful in the study of any concentrated solutions.

When we have an amalgam concentration cell, for example 2 different concentrations of thallium amalgam in contact with a solution of some thallose salt, the measured electromotive force at a given temperature depends solely upon the composition of the 2 amalgams. This must be true since all that happens in the cell of thermodynamic significance, during the passage of electric current attending the measurement of e. m. f., is the transfer of a small amount of thallium from one electrode to the other. If the concentration of thallium is very small in both amalgams, the electromotive force will be proportional to the absolute temperature, and this will continue to be the case as the concentrations are increased, until we reach the point where diluting the amalgam causes an appreciable absorption or evolution of heat. In general, the heat of the process which occurs within the cell can be determined from the electromotive force and its temperature coefficient, by means of the Helmholtz equation.

It has been assumed by several authors that the heat effect occurring within the cell and measured by the Helmholtz equation is equal to the heat of dilution, that is, to the heat evolved or absorbed when mercury is added to the more concentrated amalgam until the concentration reaches that of the more dilute amalgam. This assumption,

<sup>1</sup> Richards and Daniels, *THIS JOURNAL*, **41**, 1732 (1919).

<sup>2</sup> Hildebrand and Eastman, *ibid.*, **37**, 2452 (1915).

though erroneous in principle, gives perhaps a sufficient approximation to the truth when the amalgams are so dilute that the heat effect is small, and when available measurements are not very accurate. But in the very precise work of Richards and Forbes<sup>1</sup> this assumption led them to a calculation of the temperature coefficient of cells involving zinc amalgams, which could not be experimentally verified.

The nature of the error was perceived by Richards and Daniels, who recognized that the heat calculated by the Helmholtz equation is the heat of transfer of thallium, per mol, from one amalgam to the other, and not the heat of diluting an amount of concentrated amalgam containing one mol of thallium until the other concentration is reached. Their methods of calculating their results are, however, approximate and extremely arduous, and can be made with much greater accuracy and speed by the use of the differential calculus and the important thermodynamic properties known as the partial molal quantities.<sup>2</sup>

### The Partial Molal Quantities.

If we wish to know the change of volume in the melting of a certain amount of ice, we look up values for the molal volume, or for the specific volume, of water and of ice. If we wish to know the change of volume when a small amount of thallium is taken from one amalgam and added; to another, this difference also depends upon 2 quantities, one of which is characteristic of the one amalgam, and the other of the other.

If to any such amalgam, at constant temperature and pressure, we add a small quantity of thallium, the change of volume thus produced in the amalgam is called the partial volume of the thallium which is added, and the *rate* at which the volume changes, per mol of added thallium, is called the partial volume per mol or the partial molal volume of thallium in the amalgam of given concentration. Likewise the rate of change of the volume of the amalgam, per gram of thallium, may be called its partial volume per gram, or its partial specific volume. In a similar way we define the partial molal or the partial specific volume of mercury in the given amalgam. Both of these partial volumes will vary with the composition of the amalgam. At a given temperature and pressure, they will depend only upon the percentage composition, and not upon the total amount of amalgam considered.

Indeed in treating all physico-chemical processes which involve solutions, there is a whole set of quantities which for thermodynamic pur-

<sup>1</sup> Richards and Forbes, *Carnegie Inst. Pub.*, 56, 1 (1906); *Z. physik. Chem.*, 58, 683 (1907).

<sup>2</sup> Lewis, *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907); for other illustrations of such thermodynamic methods see the admirable paper of Brönsted, *Z. physik. Chem.*, 68, 695 (1910); also, Lewis, *THIS JOURNAL*, 34, 1631 (1912); 35, 1 (1913); Rodebush, *ibid.*, 40, 1204 (1918); Randall and Bisson, *ibid.*, 42, 347 (1920).

poses are as important, and play the same rôle, as the volume, the heat capacity, the heat content and the free energy of pure substances, and they are used in equations of identical form with those used for pure substances. Thus in addition to the partial volume, we have the partial heat capacity, partial heat content, partial free energy, etc.

### General Equations of Partial Molal Quantities.

If we have any solution, composed of  $n_1$  mols of the constituent  $X_1$  and  $n_2$  mols of the constituent  $X_2$ , and if  $G$  represents any property of the solution such as the volume, this property will depend upon the temperature, the pressure, and the amounts of the 2 constituents. Taking temperature and pressure constant,  $G$  depends upon  $n_1$  and  $n_2$ . We will define the partial molal values of  $G$ , for each constituent by the equations

$$\bar{G}_1 = \partial G / \partial n_1; \quad \bar{G}_2 = \partial G / \partial n_2. \quad (1)$$

If, starting with a given composition, we change the composition by an infinitesimal amount, we have by the fundamental equation of partial differentiation

$$dG = \frac{\partial G}{\partial n_1} dn_1 + \frac{\partial G}{\partial n_2} dn_2, \quad (2)$$

or

$$dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2. \quad (3)$$

Since  $\bar{G}_1$  and  $\bar{G}_2$  depend only upon the relative composition, and not upon the absolute amount of each constituent, we may add  $X_1$  and  $X_2$ , keeping their ratio constant, and we may integrate Equation 3,  $\bar{G}_1$  and  $\bar{G}_2$  remaining constant, so that the total  $G$  of the solution is given by the equation

$$G = n_1 \bar{G}_1 + n_2 \bar{G}_2. \quad (4)$$

Since this equation has been derived for any values of  $n_1$  and  $n_2$  we may differentiate it in a general manner and

$$dG = n_1 d\bar{G}_1 + \bar{G}_1 dn_1 + n_2 d\bar{G}_2 + \bar{G}_2 dn_2. \quad (5)$$

Combining Equations 3 and 5, we obtain the important equation which enables us to determine the rate of change of either partial  $G$  with the composition when that of the other is known, namely,

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 = 0. \quad (6)$$

Equations 4 and 6 we may refer to as the fundamental partial molal equations.

Since this equation is true for any values of  $n_1$  and  $n_2$  it is true for the special case where  $n_1 + n_2 = 1$ , that is, where  $n_1 = N_1$ , the mol fraction of  $X_1$ , and  $n_2 = N_2$  the mol fraction of  $X_2$ . Thus

$$N_1 d\bar{G}_1 + N_2 d\bar{G}_2 = 0. \quad (7)$$

If we prefer in any case to use the gram rather than the mol as our unit, all these equations hold true for the partial specific quantities if we

substitute for  $n_1$  the number of grams of a constituent, and for  $N_1$  the fraction by weight of that constituent.

### The Calculation of the Partial Molal Quantities when the Total Quantity is Known at Several Concentrations.

If we have experimental determinations of some property  $G$  over a range of compositions, we may readily determine  $\bar{G}_1$  and  $\bar{G}_2$ . We may tabulate  $G$  for solutions containing a fixed amount,  $n_2$ , of  $X_2$  and varying values of  $n_1$ . Then if we plot  $G$  against  $n_1$ , the slope of the curve at any point is  $\frac{dG}{dn_1}$  or  $\bar{G}_1$ . Similarly plotting  $G$  against varying values of  $n_2$  with constant  $n_1$ , we find  $\bar{G}_2$ .

This fundamental method of calculating partial molal quantities can be modified in numerous ways in order to utilize, without recalculation, data which happen to be given in some other form than that required for the above determination, or in order to obtain greater accuracy in the graphical work. We shall describe several such modifications in the course of this paper.

If we start with one of the constituents  $X_1$  in the pure state and add  $X_2$ , little by little, and if  $\Delta G$  is the total change in  $G$  due to the addition of the total amount of  $X_2$ , namely  $\Delta n_2$ , then  $\Delta G/\Delta n_2$  is at the outset equal to  $dG/dn_2$  and remains equal to it as long as  $dG/dn_2$  or  $\bar{G}_2$  is constant. In general, however, these 2 quantities differ. A good example of the case in which they are equal and constant is furnished by the volumes of thallium amalgams. Calling mercury  $X_1$ , and thallium  $X_2$ , the values of  $\Delta V/\Delta n_2$  are given by Richards and Daniels from 0% to 40% thallium. This quantity, which they call the "molal solution volume," has been used repeatedly by Kohlrausch<sup>1</sup> under the name of "apparent molal volume." Now in the particular case which we are considering, the apparent molal volume of the thallium over the range of investigation, and approximately within the limits of experimental error, is a constant. It is therefore equal throughout to the partial molal volume. When the apparent molal quantities are not constant, and therefore not equal to the partial molal quantities (as in the case of the heat capacity of thallium amalgams), they have very little utility in thermodynamic work, although it is sometimes desirable to calculate them as the first step in a very accurate graphic method of obtaining the partial molal quantities. This method we may now present.

**Calculation of Partial Molal Quantities by the Aid of "Apparent Molal Quantities."**—As a rule in graphic work, instead of plotting a certain quantity we may plot the small differences between this quantity and some known function, thus obtaining with less effort a higher degree of accuracy. The apparent molal quantities lend themselves well to such

<sup>1</sup> Kohlrausch. See numerous values given in the tables of Landolt and Börnstein.

employment. Such a quantity  $\Delta G/\Delta n_2$  may also be written  $\frac{G - n_1 G_1}{n_2}$  where  $G$  is, for example, the volume of an amalgam containing  $n_1$  mols of mercury and  $n_2$  mols of thallium, and  $G_1$  is the volume of one mol of pure mercury. If we plot this quantity against the common logarithm of  $n_2$ , the slope ( $s$ ) of the curve is given by the equation,

$$s = \frac{d\left(\frac{G - n_1 G_1}{n_2}\right)}{d \log n_2} = 2.303 \frac{d\left(\frac{G - n_1 G_1}{n_2}\right)}{d \ln n_2}, \quad (8)$$

where  $\ln$  represents the natural logarithm and  $d \ln n_2 = dn_2/n_2$ . Now performing the differentiation, taking  $n_1$  as constant, we find

$$\frac{s}{2.303} = \bar{G}_2 - \frac{G - n_1 G_1}{n_2}. \quad (9)$$

In other words,  $\bar{G}_2$  at any point is obtained when we divide the slope by 2.303 and add the corresponding ordinate.

We might use this method at once for the calculation of the partial molal heat capacities in thallium amalgams, since Richards and Daniels give (in their Table VIII) the apparent heat capacities. However, instead of so doing, we shall use their data to illustrate another method of obtaining partial quantities which is capable of less accuracy than the one just described, but is extraordinarily simple in its application. This method is due to Dr. R. F. Newton, of this laboratory.

**Partial Molal Quantities by the Method of Intercepts.**—It often happens that for some property  $G$  the value  $G$  for one mol of a solution is tabulated against the mol fraction (or the value for one gram against the weight per cent.). If we plot the molal value  $G$  against the mol fraction, and draw a tangent to the curve at any point, the intercept of this tangent upon the ordinate of  $N_1 = 1$  is equal to  $\bar{G}_1$  and the intercept corresponding to  $N_2 = 1$  equals  $\bar{G}_2$ .

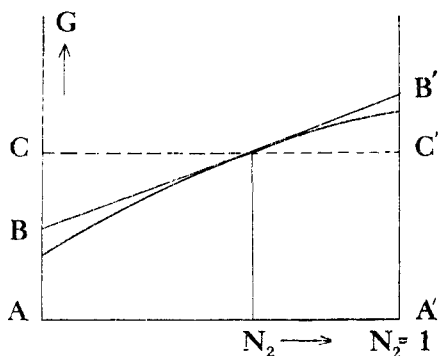


Fig. 1.

The proof of this theorem is as follows. If  $G$  is the value of some property for any amount of a solution containing  $n_1$  mols of  $X_1$  and  $n_2$  mols of  $X_2$ , then  $G$ , for one mol of the solution, is given by the equation,

$$G = G/(n_1 + n_2). \quad (10)$$

If now  $G$  is plotted as in Fig. 1 against the mol fraction  $N_2$ , namely against  $n_2/(n_1 + n_2)$ , and if we draw a tangent at any point of the curve, its slope

is  $dG/dN_2$ . The intercept AB, which we wish to prove equal to  $G_1$ , is equal to AC minus BC, and it is evident by inspection that  $AC = G$ , and  $BC = N_2 \frac{dG}{dN_2}$ , so that we must prove that

$$G - N_2 \frac{dG}{dN_2} = \bar{G}_1. \quad (11)$$

Now  $N_2$  may be varied by changing  $n_1$  or  $n_2$ , or both. For the sake of simplicity we will assume that  $n_2$  is kept constant, and that a change in  $N_2$  is produced solely by a change in  $n_1$ . We then have from Equation 10,

$$dG = \frac{dG}{n_1 + n_2} - G \frac{dn_1}{(n_1 + n_2)^2}. \quad (12)$$

Likewise,

$$dN_2 = - \frac{n_2 dn_1}{(n_1 + n_2)^2}. \quad (13)$$

Whence we find

$$N_2 \frac{dG}{dN_2} = - \frac{dG}{dn_1} + \frac{G}{n_1 + n_2} = - \bar{G}_1 + G, \quad (14)$$

which is identical with Equation 11. In the same way we prove that  $A'B'$  is equal to  $\bar{G}_2$ .

If, as is frequently the case, we find some property of a solution per gram plotted against the weight fraction, we may employ the same method and obtain the partial specific quantities which may then be converted into the partial molal quantities by multiplying by the molal weight.

**The Partial Molal Heat Capacity of Thallium and of Mercury in Thallium Amalgams.**—As an example of this mode of treatment, we may use the data of Richards and Daniels on the heat capacity of thallium amalgams. They give, in fact, just the plot which is necessary for our use, namely, the specific heat of the amalgam (heat capacity per gram) against the weight fraction of thallium. In Fig. 2, for the purpose of illustration, we have reproduced their figure with the scale extended to 100% thallium. By laying a ruler tangent to the curve at any point we read off the 2 intercepts AB and  $A'B'$ ; thus at 25 g. per cent., which is 25.3 mol per cent., we find  $AB = 0.1444$  and  $A'B' = 0.1767$ .

Since Richards and Daniels worked with joules per degree, these figures must be divided by 4.182 to convert them to calories per degree, and since moreover, these are partial specific quantities we must multiply respectively by the molal weight of mercury and of thallium in order to get the partial molal heat capacities in calories per degree. We thus find  $\bar{c}_{p1} = 6.93$  and  $\bar{c}_{p2} = 8.62$  at this composition. In the same way we read off the values given in the following table, where the first column gives the mol fraction of thallium, the second the partial molal heat capacity of the mercury, the third the partial molal heat capacity of the thallium, and

the fourth, for the sake of comparison, the apparent molal heat capacity of the thallium, as given by Richards and Daniels, and converted into our units.

TABLE I.  
Partial Molal Heat Capacities (Calories Per Degree) in Thallium Amalgams at About 20°.

N <sub>2</sub> .	$c_{p1}$ .	$c_{p2}$ .	$\frac{\Delta C_p}{\Delta n_2}$ .
0.00	6.70	10.20	...
0.05	6.72	9.81	10.13
0.10	6.75	9.54	9.90
0.15	6.80	9.15	9.66
0.20	6.85	8.82	9.45
0.25	6.93	8.62	9.27
0.30	6.97	8.50	9.12
0.35	7.02	8.40	8.96
0.40	7.05	8.34	8.81
1.00 (extrapolated)	..	8.2	...

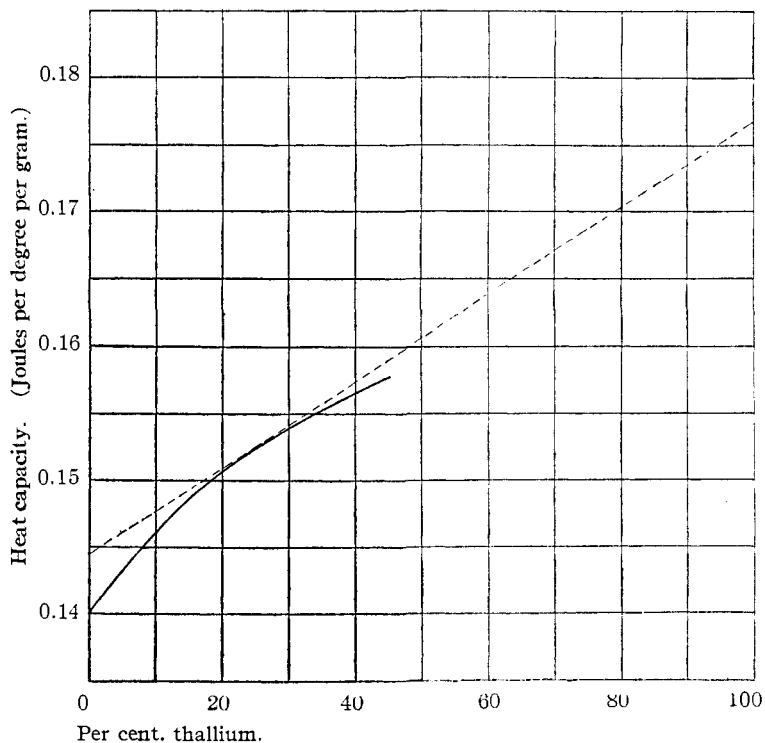


Fig. 2.—Heat capacity of thallium amalgams.

**The Calculation of Partial Molal Quantities for One Constituent when Those for the Other Constituent Are Known.**

**The Heat Content of Thallium Amalgams.**—The heat content differs from properties such as volume and heat capacity, which we have so far

considered, in that we are unable to determine the absolute heat content of any solution, and can only determine by calorimetric methods, or otherwise, the *change* in the heat content of a system when some process occurs. We may, however, obviate this dissimilarity by taking arbitrarily the heat content of each substance in some one state as zero. In the case of the thallium amalgams, at every temperature, we will call the heat content of pure mercury equal to zero, and the partial molal heat content of thallium in an infinitely dilute amalgam also equal to zero. The heat content,<sup>1</sup>  $L$ , of a given amalgam is then readily seen to be equal to the heat liberated when it is diluted with a very large amount of mercury.

Richards and Daniels made 3 independent series of measurements from which the partial heat contents in question may be calculated. In the first series they determined the heat of solution of solid thallium in various concentrations of amalgam, and in the second the heat of dilution of various amalgams from one concentration to another. From either of these series it is possible to obtain values for the partial molal heat contents of the 2 constituents of the amalgams by methods which we have already illustrated.<sup>2</sup> But the first series contains relatively large experimental errors, while the second series is also considerably more inaccurate than the very precise measurements of the third series, based upon the temperature coefficients of concentration cells. We may, therefore, give our attention entirely to this last series.

**Partial Molal Heat Content of Thallium in Various Thallium Amalgams.**—When a small current passes through the amalgam concentration cell, the whole cell will change in volume, in heat capacity, and in heat content. The change in volume per equivalent of current passed is the change in volume per mol of thallium transferred from one amalgam to the other, but this is in turn equal to the difference between the partial molal volumes of thallium in the 2 amalgams. In the same way the change of the cell in heat capacity, or heat content, or free energy, per equivalent, is obtained from the corresponding partial molal quantities of thallium. Thus from the temperature coefficient of each concentration cell Richards and Daniels obtain a quantity which is equal to the

<sup>1</sup> If for the purpose of a calculation like this, and for purely temporary convenience, we make such an arbitrary definition of the heat content, we must bear in mind that it must not be confused with the true heat content. It is for this reason that we have chosen the symbol  $L$ , instead of  $H$  which should be reserved for the true heat content. Instead of taking the partial heat content of thallium in dilute amalgam as zero we might have taken the heat content of pure solid thallium as zero, and this choice would have been almost as useful as the other.

<sup>2</sup> Thus if in place of their Fig. 9 they had plotted as ordinates, against per cent. of thallium, the heat evolved in the indefinite dilution of one gram of each amalgam, the partial specific heat contents could have been read immediately from the curve by the method of intercepts.



change in  $L_2$  between 2 concentrations, and the ordinates in their Fig. 11 (Curve H) are really the values<sup>1</sup> of  $\bar{L}_2$ , the partial molal heat content of thallium. Thus from their results we obtain the values in the second column of Table II, corresponding to the mol fractions given in the first column.

TABLE II.  
Partial Molal Heat Contents (Calories) in Thallium Amalgams at 30°.

$N_2$	$\bar{L}_2$	$\bar{L}_1$
0	0	0
0.025	212	— 3.1
0.05	413	— 10.2
0.0873	671	— 28.1
0.10	750	— 37.2
0.1070	800	— 41.8
0.15	1013	— 75.8
0.20	1195	—112
0.25	1324	—144
0.30	1415	—176
0.35	1478	—207
0.40	1520	—232
1.00 (extrapolated)	1640	...

The third column has been calculated from the second by a method which we shall now proceed to demonstrate.

#### The Partial Molal Heat Content of Mercury in Thallium Amalgams.

—If partial molal quantities for one constituent are known over a certain range of composition, the change in the corresponding partial molal quantity of the other constituent over any part of this range may be determined by a simple method of integration based upon Equation 7. For by this equation

$$\int d\bar{G}_1 = - \int \frac{N_2}{N_1} d\bar{G}_2. \quad (15)$$

If then  $\bar{G}_2$  is known and is plotted as abscissas against  $N_2/N_1$  as ordinates, the area under this curve between two limits is the change in  $\bar{G}_1$  between these limits. This procedure is illustrated in Fig. 3, where  $N_2/N_1$  is plotted

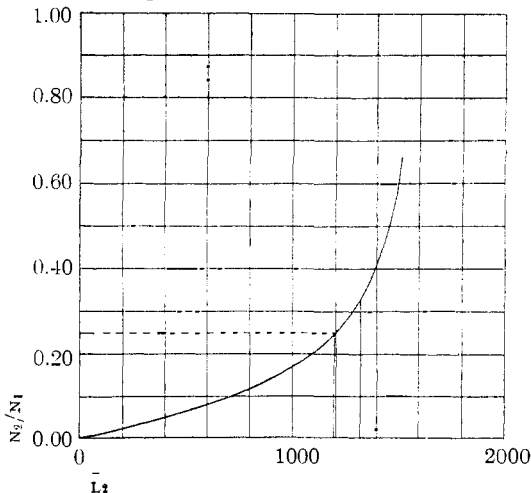


Fig. 3.—Partial molal heat content of thallium in thallium amalgams.

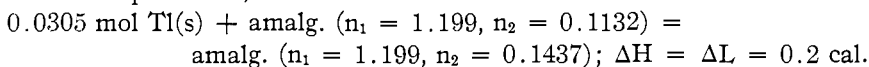
<sup>1</sup> Apparently Richards and Daniels obtain by extrapolation about 30 calories for  $\bar{L}_2$  in their most dilute amalgam (0.033%).

vertically and  $L_2$  horizontally, from the table just given. Let us consider any 2 ordinates, say  $N_2/N_1 = 0.25$  corresponding to  $N_2 = 0.20$ , and  $N_2/N_1 = 0.333$ , corresponding to  $N_2 = 0.25$ . The area under the curve between these 2 ordinates is equal to the difference in  $\bar{L}_1$  between the 2 concentrations. In other words, it is the heat effect per mol in transferring mercury from the one concentration to the other.<sup>1</sup>

Moreover, since  $L_1$  at infinite dilution is equal to  $L_1$ , the molal heat content of pure mercury, which we have taken as zero, the total area under the curve from the origin up to any given composition is the value of  $\bar{L}_1$  at that composition. By determining such areas we have obtained the values of  $\bar{L}_1$  given in Table II.

### Heat of Solution.

In discussing heats of solution in concentrated solutions there are 2 quantities which must be carefully distinguished. When a mol of thallium is dissolved in enough mercury to form a 25% amalgam, the heat absorbed is called the total or integral heat of solution. When a mol of thallium is dissolved in a very large amount of 25% amalgam the heat absorbed is called the partial or differential heat of solution. The latter quantity is the one which is the most useful in thermodynamic work. It is evidently equal to  $\bar{L}_2 - L_2(s)$ , where  $\bar{L}_2$  is the partial molal heat content of thallium in the 25% amalgam and  $L_2(s)$  is the heat content of solid thallium. We have chosen to call  $\bar{L}_2$  at infinite dilution equal to zero. Let us calculate the value of  $L_2(s)$  from the measurements of Richards and Daniels. They found that if a given amount of thallium is dissolved in a large amount of mercury, heat is evolved, but that if it is dissolved in enough mercury to give a concentrated amalgam, heat is absorbed. Probably their most accurate measurement was the one in which a very small amount of heat was absorbed, namely their Expt. 3, in which 0.0305 mol of thallium was added to an amalgam containing 1.199 mols of mercury and 0.1132 mol of thallium, to produce an amalgam containing 1.199 mols of mercury, and 0.1437 mol of thallium, with the absorption of 0.2 cal. The process is,



Let us now determine the total heat contents of these 2 amalgams, for which the mol fractions are, respectively,  $N_2 = 0.0873$  and  $N_2 = 0.1070$ . For the first amalgam, we find, from the table,  $\bar{L}_1 = -28.1$  and  $\bar{L}_2 = 671$ . But by Equation 4

<sup>1</sup> It is important to observe, and it may be readily shown, that we may obtain from this same plot the values of  $L$ , the total heat content of an amalgam of a given composition containing one mol of mercury. Thus in the figure the area between the curve, the dotted line and the vertical axis is equal to the heat content of an amalgam containing one mol of mercury and 0.25 mol of thallium. See, for example, Randall and Bisson, *loc. cit.*

$$L = n_1\bar{L}_1 + n_2\bar{L}_2$$

and  $L = 42.3$ . Likewise, for the second amalgam,  $L = 64.8$ . Hence by the law of conservation of energy

$$64.8 - 0.0305 L_2(s) - 42.3 = 0.2; L_2(s) = 730 \text{ cal.}$$

This is the heat evolved when one mol of thallium dissolves in an infinite amount of mercury. Or, expressing this result in still another form,

$$\text{Tl}(s) = \text{Tl}(\text{in Hg}, N_2 = 0); \Delta H = -730.$$

If instead of Expt. 3 of Richards and Daniels, we had used the sum of Expts. 3, 4, 5, 6 and 7, we should have found  $L_2(s) = 720$ . In fact, the uncertainty of the experimental data leads to a probable error of the order of magnitude of 20 calories in  $L_2(s)$ , and we may take  $L_2(s) = 730 \pm 20$  cal.

As a final illustration of the methods of utilizing total heat contents we may calculate a quantity which was measured by Richards and Daniels, but by a method in which they had little confidence; namely, the integral heat of solution of 0.1132 mol of thallium in 1.199 mols of mercury, to give the first amalgam of the preceding illustration. The heat content of that amalgam was found to be 42.3, that for the thallium is  $(730 \pm 20) \times 0.1132$ , that of the mercury we have taken as 0, hence  $\Delta H = -40.3 \pm 2$  cal or  $-169 \pm 8$  joules. This is a more accurate determination than the direct one of Richards and Daniels for which they give the round value of  $-200$  joules.

#### Change of Heat of Transfer with the Temperature.

If we consider the transference of a small amount of thallium or of mercury from one amalgam to another, we have only to consider the partial molal quantities in the 2 amalgams. Thus, if we consider the heat of transfer of thallium, per mol, from an amalgam of 10 mol per cent. to one of 40 mol per cent. of thallium, we find from Table II the values of  $\bar{L}_2$ , namely 750 and 1520, and we write for  $30^\circ \text{C} = 303^\circ \text{A}$ ,

$$\text{Tl}(\text{in Hg}, N_2 = 0.10) = \text{Tl}(\text{in Hg}, N_2 = 0.40);$$

$$\Delta H_{303} = \Delta L = 1520 - 750 = 770 \text{ cal.}$$

Now we have the general equation

$$d(\Delta H)/dT = \Delta C_p \quad (16)$$

where  $\Delta C_p$  is the difference in the partial molal heat capacity of thallium of the 2 amalgams. This quantity we find from Table I to be  $8.34 - 9.54 = -1.2$  calories per degree.

Similarly, we find from Tables I and II, for the transfer of mercury (per mol) from pure mercury to an amalgam in which  $N_2 = 0.40$ ,

$$\text{Hg}(l) = \text{Hg}(\text{in Tl amalg.}, N_2 = 0.40);$$

$$\Delta H_{303} = -232 - 0 = -232; \Delta C_p = 7.05 - 6.70 = 0.35.$$

We shall use these values in a later calculation.

### Partial Molal Free Energy and Activity.

The free energy change, per equivalent, in the transfer of thallium from one amalgam to another is obtained immediately from the e. m. f. of the concentration cell. It is equal to the difference between the values of  $\bar{F}_2$ , the partial molal free energy of the thallium, for the 2 concentrations. We might proceed, as in the previous sections, to determine, between 2 concentrations, the change in  $\bar{F}_1$ , the partial molal free energy of the mercury. But while the general equations for partial molal free energy are of course the same as those for other partial quantities, the numerical calculations are altered by the fact that the partial free energy of a solute approaches an infinite value as the concentration is diminished. For this reason new devices are necessary for expediting the numerical calculations.

One of the most important of these devices consists in the introduction of the function called the activity,  $a$ , which is so defined that if  $\bar{F}_2 - \bar{F}_2'$  is the change in free energy per mol, in transferring the constituent  $X_2$  from one concentration to another, and if this constituent has the activity  $a_2$  in the one state and  $a_2'$  in the other, then

$$\bar{F}_2 - \bar{F}_2' = RT \ln \frac{a_2}{a_2'}, \quad (17)$$

or

$$d\bar{F}_2 = RT d \ln a_2. \quad (18)$$

The activity thus becomes a function which has the advantage of never becoming infinite, and the further advantage that in the ideal or perfect solution  $a_1$  is proportional to  $N_1$ , and  $a_2$  to  $N_2$ . We may moreover choose arbitrarily the value of  $a$  for each constituent in some one state, and in the case which we are here considering we shall take for pure mercury  $a_1 = 1$  or, in the infinitely dilute solution,  $a_1/N_1 = 1$ ; and for thallium we shall make  $a_2/N_2 = 1$  at infinite dilution. Our problem now resolves itself into the problem of determining the activities of the two constituents at various concentrations.

From Equation 7 we have at constant temperature,

$$d\bar{F}_1 = - \frac{N_2}{N_1} d\bar{F}_2, \quad (19)$$

and

$$d \ln a_1 = - \frac{N_2}{N_1} d \ln a_2. \quad (20)$$

If we wish we may use common instead of natural logarithms, and by integrating

$$\int d \log a_1 = - \int \frac{N_2}{N_1} d \log a_2. \quad (21)$$

If then we know values of  $a_2$  and plot their logarithms against  $N_2/N_1$ , the

area between any 2 limits gives the change in  $-\log a_1$  between these limits.

We may, however, improve the accuracy of the graphical method by a simple expedient. Noting that for the mol fractions,  $N_1 + N_2 = 1$  and  $dN_1 = -dN_2$ , we see that

$$d \ln N_1 = \frac{dN_1}{N_1} = -\frac{dN_2}{N_1} = -\frac{N_2}{N_1} d \ln N_2. \quad (22)$$

Subtracting this from Equation 20

$$d \ln \frac{a_1}{N_1} = -\frac{N_2}{N_1} d \ln \frac{a_2}{N_2} \quad (23)$$

or as before

$$\int d \log \frac{a_1}{N_1} = - \int \frac{N_2}{N_1} d \log \frac{a_2}{N_2}. \quad (24)$$

Those who have worked in this branch of applied thermodynamics will recognize immediately the extreme importance of an equation which not merely permits such a calculation of the ratio of 2 values of  $a_1$  between 2 finite concentrations, but which permits extrapolation to zero concentration, and hence the evaluation of individual values of  $a_1$ . Equation 24 is admirably adapted for such purpose,<sup>1</sup> for in very dilute solution both  $a_1/N_1$  and  $a_2/N_2$  are unity, and in concentrated solutions they differ from unity only insofar as the solution differs from the perfect solution. Such an equation is therefore very advantageous, not only for extrapolation, but for any graphical treatment. The use of equations of this type will be illustrated in the following sections.

### The Activity of Thallium in Amalgams from the Electromotive Force of Concentration Cells.

The relation between the change of free energy and the electromotive force of a cell is given by the equation

$$-\Delta F = NFE \quad (25)$$

where for a concentration cell  $\Delta F$  is the change of free energy accompanying the transfer of one mol,  $E$  is the electromotive force,  $F$  is the value of the faraday, and  $N$  is the number of faradays per mol transferred. In the case of the thallium amalgams  $N = 1$ , and combining (25) with (17),

$$\ln \frac{a_2}{a'_2} = -\frac{FE}{RT}, \quad (26)$$

and at 20°, using common logarithms,

$$\log \frac{a_2}{a'_2} = \frac{-E}{0.05816}. \quad (27)$$

<sup>1</sup> For a similar solution of an analogous problem see Lewis and Linhart, THIS JOURNAL, 41, 1951 (1919).

Now let  $N_2$  be the mol fraction and  $a_2$  the activity of thallium in any amalgam, and  $N'_2$  and  $a'_2$  the corresponding values in some particular amalgam chosen for reference. Then  $E$  is the electromotive force of any concentration cell of which one electrode is the amalgam of fixed mol fraction  $N'_2$ , and the other is an amalgam of any mol fraction  $N_2$ . Subtracting  $\log N_2$  from both sides of Equation 27 we have

$$\log \frac{a_2}{N_2} = \left( \frac{-E}{0.05816} - \log N_2 \right) + \log a'_2. \quad (28)$$

If now we plot the quantity in parenthesis against  $N_2$ , as in Fig. 4, we have a very simple and exact method of interpolating and extrapolating the experimental results. When  $N_2 = 0$ , we have by definition  $a_2/N_2 = 1$ , or  $\log (a_2/N_2) = 0$ . The value of the ordinate where the curve cuts the vertical axis is therefore equal to  $-\log a'_2$ , and this value subtracted from the ordinate at any other value of  $N_2$  gives at once  $\log (a_2/N_2)$  at that point.

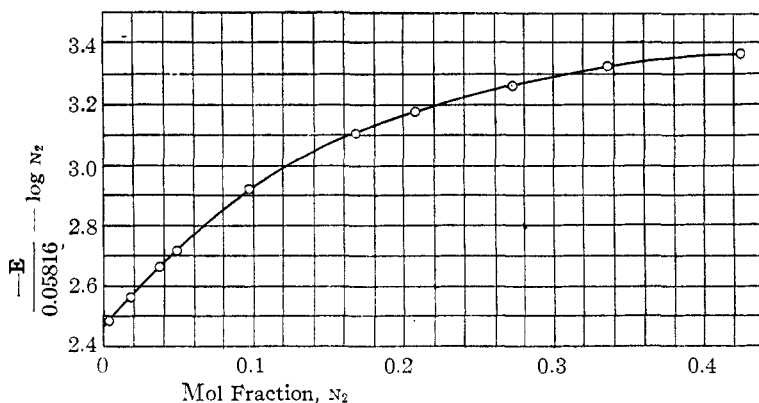


Fig. 4.

Table III gives Richards and Daniels' experimental results for the electromotive force of thallium amalgam concentration cells. The first column gives  $N_2$ , the mol fraction of thallium. The second gives their e. m. f. (which is our  $-E$ ) at  $20^\circ$  between an amalgam of the mol fraction given, and the most dilute amalgam,  $N'_2 = 0.00326$ . The next column gives  $\left( \frac{-E}{0.05816} - \log N_2 \right)$  which is plotted as ordinate in Fig. 4.

the fourth gives the values of  $a_2/N_2$  obtained from the plot by the method just described. Namely,  $\log (a_2/N_2)$  is obtained by subtracting the intercept on the axis of ordinates,  $-\log a'_2 = 2.4689$ , from the values in Col. 3. The last column<sup>1</sup> gives the values of  $a_2$ .

<sup>1</sup> The value of  $a_2$  for solid thallium is obtained directly by the aid of Equation 26. It is to be noted that Lewis and von Ende (*THIS JOURNAL*, **32**, 732 (1910)), assumed the potential of solid thallium to be the same as that of a saturated thallium amalgam,

TABLE III.  
Activities of Thallium in Amalgams at 20°.

$N_2$ .	$-\frac{E}{\text{volts.}}$	$\left(\frac{-E}{0.05816} - \log N_2\right)$ .	$\frac{a_2}{N_2}$ .	$a_2$ .
0	$-\infty$	2.4689	1	0
0.003259	0	2.4869	1.042	0.003396
0.01675	0.04555	2.5592	1.231	0.02062
0.03723	0.07194	2.6660	1.574	0.05860
0.04856	0.08170	2.7184	1.776	0.08624
0.0986	0.11118	2.9177	2.811	0.2772
0.1680	0.13552	3.1045	4.321	0.7259
0.2074	0.14510	3.1780	5.118	1.061
0.2701	0.15667	3.2610	6.196	1.674
0.3361	0.16535	3.3159	7.031	2.363
0.4240	0.17352	3.3558	7.707	3.268
Tl (solid)	0.1763	..	...	3.650
Tl (liquid, supercooled) <sup>a</sup>	..	..	8.3	8.3

<sup>a</sup> It will be observed that in the higher concentrations the values of  $a_2/N_2$  are rapidly approaching a constant value, about 8.3. This value will give  $a_2/N_2$  for pure supercooled liquid thallium, a quantity which we might have taken as unity if we had not already chosen to regard thallium as the solute, and to write  $a_2/N_2 = 1$  in the dilute amalgam. It is only in the case of the solution which is perfect at all concentrations that  $a_2/N_2$  when  $N_2 = 0$ , is the same as  $a_2/N_2$  when  $N_2 = 1$  or, in other words, that the constant of Henry's law is the same as the constant of Raoult's law.

### The Activity of Mercury in Thallium Amalgams at 20°.

From the data of Table III we may plot  $N_2/N_1$  as ordinates against  $\log (a_2/N_2)$  as abscissas and obtain the curve of Fig. 5. Using Equation 24, and remembering that  $a_1/N_1 = 1$  and  $\log a_1/N_1 = 0$ , when  $N_2/N_1 = 0$ , the area under this curve up to a given value of  $N_2/N_1$  is equal to  $-\log (a_1/N_1)$  at that composition.<sup>1</sup> We thus find at round mol fractions the values of  $a_1/N_1$  given in the last column of Table IV. The corresponding values of  $a_2/N_2$  are given for reference.<sup>2</sup>

since at ordinary temperatures thallium and mercury had been shown by Kurnakov and Puschkin to form no compound, and since Sucheni had shown that mercury does not dissolve appreciably in solid thallium. Richards and Daniels find by preliminary experiment that the saturated amalgam has a lower potential than pure thallium by 0.0025 volt. If this result was not due to the use of solid thallium in some state of strain, then the statement of Sucheni must be incorrect, and solid thallium must dissolve several per cent. of its own weight of mercury.

<sup>1</sup> In Fig. 4 we might equally well have plotted  $\left(\frac{-E}{0.05816} - \log N_2\right)$  against some function of  $N_2$  instead of against  $N_2$  itself. If we had plotted not  $N_2$  but  $N_2/N_1$  we should have obtained a curve of about the same appearance. With such a figure, we could at once have obtained  $\log (a_1/N_1)$  without obtaining  $\log (a_2/N_2)$ , merely by determining the area, to the left of the curve from  $N_2/N_1 = 0$ , up to a given abscissa, thus entirely avoiding the necessity of drawing the curve of Fig. 5.

<sup>2</sup> These figures in the third column have been interpolated with an accuracy of only about 1%.

TABLE IV.

Activity of Mercury (and of Thallium) in the Amalgams at 20°.

$N_2$ .	$N_2/N_1$ .	$a_2/N_2$ .	$a_1/N_1$ .
0	0	1	1
0.005	0.00502	1.06	0.9998
0.01	0.0101	1.15	0.999
0.05	0.0526	1.80	0.986
0.1	0.111	2.84	0.950
0.2	0.250	4.98	0.866
0.3	0.428	6.60	0.790
0.4	0.667	7.57	0.734
0.5	1.000	7.98	0.704

**The Calculation of the Activities from Vapor Pressure Measurements.**

Hildebrand and Eastman have measured at 325° the vapor pressure

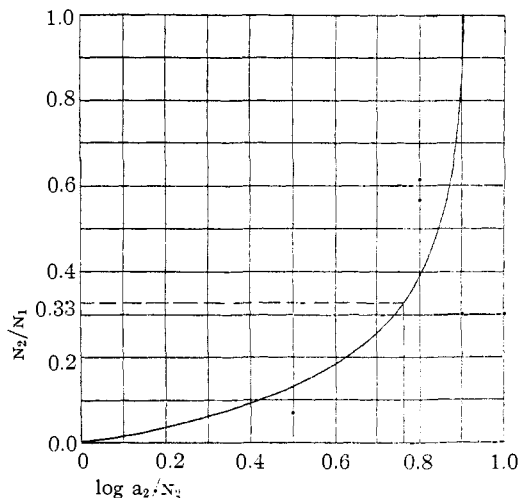


Fig. 5.—Activity of thallium in thallium amalgams at 20°.

of mercury from various thallium amalgams. If we assume that mercury vapor acts like a perfect gas, an assumption which is in all probability correct within the limits of experimental error, the activity of the mercury is proportional to its vapor pressure. Thus if, at the given temperature,  $p_1$  is the vapor pressure of mercury from an amalgam of any concentration, and  $p_1^\circ$  is that of pure mercury, then since we take  $a_1 = 1$  for pure mercury,

$$a_1 = \frac{p_1}{p_1^\circ}; \quad \frac{a_1}{N_1} = \frac{p_1}{N_1 p_1^\circ}. \quad (29)$$

Thus the values of  $p_1/p_1^\circ$  given by Hildebrand and Eastman, when divided by  $N_1$ , furnish directly values of  $a_1/N_1$ . We may now exchange the subscripts in Equation 24 in order to obtain an equation for determining  $a_2/N_2$  when  $a_1/N_1$  is known, namely,

$$\int d \log \frac{a_2}{N_2} = - \int \frac{N_1}{N_2} d \log \frac{a_1}{N_1}. \quad (30)$$

Here we might perform a graphical integration as before. Since, however, in any such integration we have the choice of using an analytical instead of a graphical method, and since Hildebrand and Eastman have



already used just such an analytical method very successfully, in the interpretation of their results, we may make use of the empirical equation which they obtain, namely,

$$\log \frac{P_I}{P_I^0} = \log N_1 - \frac{0.0960}{\left(1 + 0.263 \frac{N_1}{N_2}\right)^2}, \quad (31)$$

which can be written

$$\log \frac{a_1}{N_1} = - \frac{0.0960}{\left(1 + 0.263 \frac{N_1}{N_2}\right)^2}. \quad (32)$$

Substituting in (30) and integrating<sup>1</sup>

$$\log \frac{a_2}{N_2} = \frac{2 \times 0.0960}{0.263} \left( \frac{1}{1 + 0.263 \frac{N_1}{N_2}} - \frac{1}{2 \left(1 + 0.263 \frac{N_1}{N_2}\right)^2} \right) \quad (33)$$

From Equations 32 and 33 we have obtained the values given in Table V.<sup>2</sup>

TABLE V.<sup>a</sup>  
Activities of Mercury and Thallium in Amalgams at 325°.

$N_2$	$\frac{a_1}{N_1}$	$\frac{a_2}{N_2}$
0	1	1
0.10	0.98	1.53
0.20	0.95	1.86
0.30	0.92	2.05
0.40	0.89	2.17
0.50	0.87	2.23
0.60	0.85	2.28
0.70	0.83	2.30
0.80	0.82	2.31
(1.00)	(0.80)	(2.32)

<sup>a</sup> It will be observed from this table and several of the others, how much more nearly the thallium amalgams behave like perfect solutions when there is an excess of thallium than when there is an excess of mercury. This is quite in accord with the idea of Hildebrand and Eastman that the chief cause of the departure of these amalgams from the laws of the perfect solution is the formation of a compound containing more molecules of mercury than of thallium.

<sup>1</sup> The fundamental equation for the integration is,

$$\int \frac{x dx}{(1 + cx)^3} = \int \frac{1}{c^2} \left( \frac{-1}{1 + cx} + \frac{1}{2(1 + cx)^2} \right).$$

<sup>2</sup> If we had used the graphical method of extrapolation and used the smoothed out values given by Hildebrand and Eastman, we should of course have obtained the same values for  $a_2/N_2$  as those given in the table. On the other hand, if we had given full weight to their experimental values at their 2 lowest concentrations, where errors of measurement are greatly exaggerated, we would have found a different extrapolation and considerably lower values of  $a_2/N_2$ , but differing from those of the table by a constant factor.

The last figures in parenthesis are the extrapolated values for  $N_2 = 1$ ; in other words, 2.32 is the activity of pure molten thallium, and 0.80 is the value of  $a_1/N_1$  in a very dilute solution of mercury in thallium, when the activity of pure mercury is taken as unity.

#### Comparison of the Activities at 20° and 325°.

It is now a simple matter to calculate from the vapor pressures of mercury over the amalgams at 325°, the electromotive force of the concentration cells at 20°, or *vice versa*. This is the same in principle as the comparison of the activity values obtained at the 2 temperatures.

For any process we have the fundamental thermodynamic equation

$$d\left(\frac{\Delta F}{T}\right) = -\frac{\Delta H}{T^2}, \quad (34)$$

where  $\Delta F$  is the increase in free energy and  $\Delta H$  is the increase in the heat content attending the process. Let us consider the values of these quantities per mol when at a given temperature one of the constituents, for example thallium, is transferred from one amalgam to the other. Then

$$\Delta F = \bar{F}_2 - \bar{F}'_2 = RT \ln \frac{a_2}{a'_2}, \quad (35)$$

and

$$\Delta H = \bar{L}_2 - \bar{L}'_2. \quad (36)$$

Whence Equation 34 becomes

$$dR \ln \frac{a_2}{a'_2} = -\frac{\Delta H}{T^2} dT = -\frac{\bar{L}_2 - \bar{L}'_2}{T^2} dT. \quad (37)$$

Since we wish to consider the transfer from an amalgam of one given composition to an amalgam of another given composition, at various temperatures, we shall take  $N_2$  and  $N'_2$  as constant, and may then, for later convenience, write in place of Equation 37,

$$dR \ln \frac{a_2 N'_2}{a'_2 N_2} = -\frac{\Delta H}{T^2} dT = -\frac{\bar{L}_2 - \bar{L}'_2}{T^2} dT. \quad (38)$$

Now in order to find how the ratio  $a_2/a'_2$  changes with the temperature we must integrate Equation 37 or 38, and this can only be done when we have complete knowledge of  $\Delta H$  as a function of the temperature. For integration over a small range, it is usually sufficiently accurate to take  $\Delta H$  as constant; over a wider range it is desirable to know the first derivative of  $\Delta H$  with the temperature, a quantity which is known when the proper heat capacities have been determined. Thus in the case before us we have by Equation 16,

$$\frac{d(\Delta H)}{dT} = \Delta C_p,$$

or,

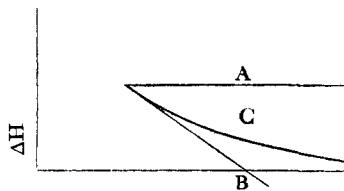
$$\frac{d(\bar{L}_2 - \bar{L}'_2)}{dT} = \bar{c}_{p_2} - \bar{c}'_{p_2}, \quad (39)$$

and if the second member is taken as constant  $\Delta H$  may be expressed as a linear function of the temperature. However, over a still wider range it is hardly safe to assume  $\Delta C_p$  to be constant, especially if, in spite of a lack of any direct experimental evidence, we have good reason to believe that  $\Delta C_p$  not only changes markedly with the temperature, but in a direction which may be foretold.

This is the case, not only in the particular problem before us, but also in nearly all analogous problems where we deal with solutions. It is therefore desirable to abandon for a moment the purely thermodynamic mode of treatment to consider certain rough generalizations, which rest partly upon theoretical but chiefly upon an empirical basis.

**The Effect of Temperature upon the Abnormality of Solutions.**—A perfect solution is defined as one in which such properties as volume, heat capacity and heat content are determined additively by the properties of its pure constituents. Insofar as a given solution departs from the perfect solution, the degree of departure may be roughly termed its abnormality. It is a fact of common observation that the abnormality of solutions diminishes with increasing temperature. It is true that rare cases are known of very abnormal solutions which at first become more abnormal with rising temperature, although they too obey the general rule at yet higher temperatures. In any ordinary case we may assume that the abnormality of a solution is diminishing gradually with increasing temperature, and in such manner as to approach zero as the temperature is indefinitely increased.

Thus in fact we find that when in a given solution there is a finite heat of dilution, the heat capacities are of such sign and magnitude that the heat of dilution diminishes with increasing temperature. For one of the components  $X_2$ , of a perfect solution, we have between any 2 concentrations  $\bar{L}_2 - \bar{L}'_2 = 0$  and  $\bar{c}_{p_2} - \bar{c}'_{p_2} = 0$ . Now if the solution is not perfect, we assume that these quantities approach zero as the temperature is increased. According to this assumption, if we plot  $\bar{L}_2 - \bar{L}'_2$  against the temperature, we should have such a curve as the one marked (C) in Fig. 6, a curve for which not only the ordinate but the slope must approach zero as  $tT = \infty$ , for by Equation 39 that slope is equal to  $\bar{c}_{p_2} - \bar{c}'_{p_2}$ . If we had assumed  $\Delta H$  constant we should have the straight line marked (A) in Fig. 6, while if we assume  $\bar{c}_{p_2} - \bar{c}'_{p_2}$  constant, we get such a line as the one marked (B), which would make  $\Delta H$  zero at some finite temperature, beyond which its value would rapidly in-



Absolute Temperature, T.

Fig. 6.

crease numerically with increasing temperature. We will reserve for another communication the discussion of the most probable form of the curve (C) and merely note for our present purpose that the actual behavior of a solution will be intermediate between that postulated upon the assumption of constant  $\Delta H$  and that postulated upon the assumption of constant  $\Delta C_p$ .

If then we know both  $\Delta H$  and  $\Delta C_p$  at the lower end of our temperature range, and if we first make a calculation based upon the assumption of constant  $\Delta H$  and then make the calculation based upon constant  $\Delta C_p$  the truth will be somewhere between the results so obtained. We will illustrate this point by continuing our discussion of the thallium amalgams.

#### Calculation of the Activities of Thallium in Amalgams at 325°.

Let us consider first the transfer of thallium from an amalgam in which  $N_2 = 0.10$ , to one in which  $N_2 = 0.40$ . In the first instance we will assume  $\Delta H = \bar{L}_2 - \bar{L}_2'$  to be constant, where the integration of Equation 38 gives

$$R \ln \frac{a_2 N_2'}{a_2' N_2} = 2.303 R \log \frac{a_2 N_2'}{a_2' N_2} = \frac{\Delta H}{T} + J, \quad (40)$$

where  $J$  is the constant of integration. From Table IV we find at 20° C. or 293° A,  $a_2/N_2 = 7.57$  and  $a_2'/N_2' = 2.84$ . From Table II,  $\Delta H = \bar{L}_2 - \bar{L}_2' = 1520 - 750 = 770$  cal. Substituting these values and  $T = 293$  we find  $J = -0.678$ . Using this value at 325° C. or 598° A we find  $a_2/N_2 = 1.36 a_2'/N_2'$ .

Now we make the same calculation taking  $\Delta C_p$  from Table I and assuming it to be constant. Then

$$\Delta H = \Delta H_0 + \Delta C_p T, \quad (41)$$

where  $\Delta H_0$  is a constant. Substituting in Equation 38 and integrating,

$$2.303 R \log \frac{a_2 N_2'}{a_2' N_2} = \frac{\Delta H}{T} - 2.303 \Delta C_p \log T + J. \quad (42)$$

From Table I,  $\Delta C_p = \bar{c}_{p_2} - \bar{c}_{p_2}' = 8.34 - 9.54 = -1.20$ . Substituting this in Equation 41 and  $\Delta H_{303} = 770$ , we find  $\Delta H_0 = 1134$ , and using for the first member of the equation the same value as before, we find  $J = -8.736$ , and at 598° A,  $a_2/N_2 = 1.53 a_2'/N_2'$ .

Thus for the ratio, at the 2 chosen concentrations, of  $a_2/N_2$  to  $a_2'/N_2'$  we find by the first method (assuming  $\Delta H$  constant) 1.36, by the second method (assuming  $\Delta C_p$  constant) 1.53, while the ratio obtained from the measurements of Hildebrand and Eastman as interpreted in Table V gives the intermediate value 1.42.

**Calculation of the Activity of Mercury in Amalgams at 325° C.**—Let us now take an entirely similar calculation for the transfer of mercury from pure mercury, where  $N_2 = 0$ , to the amalgam of  $N_2 = 0.40$ . Here,

by definition,  $a'_1/N'_1 = 1$ . From Table II  $\Delta H_{303} = -232$ , from Table I  $\Delta C_p = 7.05 - 6.70 = 0.35$ , from Table IV  $a_1/N_1 = 0.734$ , and making all calculations precisely as in the case of the thallium we find at  $598^\circ\text{A}$  by the first method ( $\Delta H$  assumed constant)  $a_1/N_1 = 0.899$ , by the second method ( $\Delta C_p$  assumed constant)  $a_1/N_1 = 0.871$ , while from the measurements of Hildebrand and Eastman (Table V) we find 0.89. This is a more satisfactory agreement than the previous one, owing to the fact that the thermal quantities involved are smaller and subject to less uncertainty. In this last calculation we are really calculating the vapor pressure or  $p_1/p_1^\circ$  at the high temperature from the measurements of electromotive force at the low temperature. Thus  $p_1/p_1^\circ$  would be 0.60 from Raoult's law, is found to be 0.534 by Hildebrand and Eastman, while we obtain 0.539 and 0.522 by our 2 methods.

### The Heat of Fusion of Thallium.

Finally, in order to show how we may use the extrapolated values which we have given in several tables for the properties of pure liquid thallium in a supercooled condition, we shall make 2 rough calculations of the heat of fusion of solid thallium at its melting point, which is about  $300^\circ\text{C}$ ., or  $573^\circ\text{A}$ .

Considering the process  $\text{Tl}(s) = \text{Tl}(l)$ , we have found at ordinary temperatures, for liquid thallium (Table I)  $c_p = 8.2$ , and for solid thallium the literature gives about 6.2. Whence  $\Delta C_p = 2.0$ . At  $303^\circ\text{A}$  we have found values for the heat contents (Table II *et seq.*), namely for liquid  $L_2 = 1640$ , and for solid  $L_2 = 730$ . Whence  $\Delta H_{303} = 910$ . Thus from the equation

$$\Delta H = \Delta H_o + 2.0T$$

$\Delta H_{573} = 1450$  cal. The only direct measurement of this heat of fusion which we find is that of Robertson,<sup>1</sup> namely 1470.

Even if we had no calorimetric values for the heat contents and had only the electromotive forces of the concentration cells at one temperature we could still make an estimate of this heat of fusion. For at  $20^\circ\text{C}$ . from Table III, for liquid thallium  $a_2$  is about 8.3 and for solid is 3.65, while at the melting point the 2 activities are identical. Using the same equations ( $\Delta C_p$  constant) as in the preceding section, but reversing our procedure so as to make  $\Delta H_o$  the quantity for which we solve, we find  $\Delta H_o = 180$  and  $\Delta H_{573} = 1326$ , a somewhat smaller value than the other two, and undoubtedly less accurate.

### Summary.

Having developed numerous methods for the thermodynamical treatment of concentrated solutions, and for the rapid and precise calculation of partial molal quantities, these methods have been applied to the data

<sup>1</sup> Robertson, *Proc. Chem. Soc.*, 18, 131 (1903).

for thallium amalgams obtained by Richards and Daniels and by Hildebrand and Eastman. It has been shown how the heat of solution of solid thallium and of supercooled liquid thallium in a large excess of mercury may be obtained, and later how these quantities may be used for calculating the heat of fusion of thallium. The activities of thallium and of mercury in amalgams of various compositions are given at 20° C. and at 325° C., and these values, resting upon independent measurements, are compared by simple thermodynamic methods. The effect of temperature upon the abnormality of solutions is discussed, and it is shown that the vapor pressure of amalgams at 325° may be calculated from the measurement of electromotive force at 20° by 2 methods, between which 2 results the true value must lie. Thus in 40% amalgam the vapor pressure was found by one method to be 1% higher and by the other to be 2% lower than the measured value.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

## THE DISTRIBUTION OF A STRONG ELECTROLYTE BETWEEN BENZENE AND WATER.

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In the effort to determine the degree of dissociation of a strong electrolyte in water, distribution experiments should be of use. Such experiments have rarely been performed, probably because of the difficulty in finding strong electrolytes which possess suitable solubility in a non-aqueous solvent which is itself immiscible with water. The distribution of picric acid between water and benzene has been studied by Kuriloff,<sup>1</sup> Walden,<sup>2</sup> Rothmund and Drucker,<sup>3</sup> and Herz and Fischer,<sup>4</sup> and that of lithium chloride between water and amyl alcohol by Dhar and Data.<sup>5</sup> Other cases have not been found.

The theory by which such experiments may be interpreted is well known. According to Berthelot and Jungflesch<sup>6</sup> and as elaborated by Nernst,<sup>7</sup> the distribution law states that a solute will be partitioned between 2 immiscible solvents in a ratio which is independent of the concentrations used, and which is the ratio of its solubility in the 2 pure solvents, provided that the solvents are immiscible in each other, that the

<sup>1</sup> Kuriloff, *Z. physik. Chem.*, **25**, 425 (1898).

<sup>2</sup> Walden, *Ber.*, **34**, 419 (1901).

<sup>3</sup> Rothmund and Drucker, *Z. physik. Chem.*, **46**, 827 (1903).

<sup>4</sup> Herz and Fischer, *Ber.*, **37**, 4746 (1904); *ibid.*, **38**, 1138 (1905).

<sup>5</sup> Dhar and Data, *Z. Elektrochem.*, **19**, 583 (1913).

<sup>6</sup> Berthelot and Jungflesch, *Ann. chem. phys.*, [4] **26**, 396 (1872).

<sup>7</sup> *Z. physik. Chem.*, **8**, 110 (1891).